

A STUDY OF WELL WATER IN SELECTED CALIFORNIA  
COMMUNITIES FOR RESIDUES OF 1,3-DICHLOROPROPENE,  
CHLOROALLYL ALCOHOL AND 49 ORGANOPHOSPHATE OR CHLORINATED  
HYDROCARBON PESTICIDES

By

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Liquid cis- and trans-1,3-dichloropropene is a soil applied nematicide registered for use on numerous crops grown in California. The most widely used pesticide formulations containing 1,3-dichloropropene include Telone (Dow Chemical Co.) and D-D (Shell Chemical Co.). Major areas of use of 1,3-dichloropropene in California have been the San Joaquin Valley and the coastal counties of Monterey and Santa Barbara. Crops for which 1,3-dichloropropene treatments have been used include cotton, tomatoes, sugarbeets, broccoli, alfalfa, Brussels sprouts, and other field, fruit and various vegetable crops. Application is usually by injection into the soil at a depth of 6 inches using tractor mounted injection equipment.

Since the suspension of DBCP (1,2-dibromo-3-chloropropane) registrations in California in mid-1977, 1,3-dichloropropene has been considered as an alternative nematicide for use in established crop areas. Experimental applications on established crops including grapes, almonds and peaches, have been conducted to evaluate phytotoxicity, efficacy and worker exposure data under post-planting conditions.

Skin and eye contact with concentrated 1,3-dichloropropene can result in severe irritation with possible edema and necrosis of the exposed area. Extensive exposure can lead to nausea, vomiting, pulmonary edema, liver and kidney damage, anesthesia, and death, though no human deaths have been reported due to 1,3-dichloropropene exposure. Microbial assays have shown 1,3-dichloropropene to be a mutagen (STOLZENBERG and HINES, 1980; NEUDECKER, et al., 1977).

The potential for groundwater contamination from chemicals applied primarily to soil is a major public health concern. DBCP and 1,3-dichloropropene are structurally similar. Cis- and trans-chloroallyl alcohols, primary degradation products of 1,3-dichloropropene, may persist and become groundwater contaminants. It has been reported that high soil concentrations of 1,3-dichloropropene (62-250 ppm) interfered with microbial degradation of chloroallyl alcohol (BAINES, et al., 1977). Toxicity data are nearly nonexistent on chloroallyl alcohol, however the chloroallyl moiety is common to a number of mutagenic chemicals.

## MATERIALS AND METHODS

Wells selected for the study were primarily municipal supply systems for urban and residential use. Selections were based on the proximity to areas where Telone or D-D had been applied for several years. High-use areas were identified from the annual California Pesticide Use Reports (1975 to 1980) and discussions with local farm advisors.

Well locations were provided by the Sanitation Engineering Section of the California Department of Health Services. Depth of each well was obtained from the owner or operator. Well depths are summarized in Table 1.

All well water samples were analyzed for 1,3-dichloropropene, and a number of organophosphate and chlorinated hydrocarbon pesticides, which are listed in Tables 3 and 4. Selected samples, located in the communities of Ripon, Manteca, Firebaugh, San Joaquin, Tranquility, Atwater, and Livingston were analyzed for chloroallyl alcohol.

Sampling containers were 1-quart mason jars that were washed, rinsed with acetone then distilled water, and heated for 12 hours at 160° C. The person collecting the samples wore disposable polyethylene gloves and exchanged these for each sample.

Samples were drawn from a faucet situated between the pump and storage tank after the pump had been operating for at least one minute. Sample jars were filled, leaving as little headspace as possible, then capped with a sheet of aluminum foil and a jar lid. Samples were chilled on wet ice and analyzed within 72 hours of collection.

Dichloropropene was extracted from water by co-distillation with ethyl acetate. The extract was shaken with a small amount of anhydrous sodium sulfate to remove excess water, then analyzed by electron-capture detector (ECD) gas chromatography.

Chloroallyl alcohol was extracted from water by partitioning into diethyl ether. The ether extract was passed through a bed of anhydrous sodium sulfate, then evaporated to near dryness. The residue was redissolved in hexane before analysis by gas chromatography using a Hall electro-conductivity detector (HECD).

Chlorinated hydrocarbons and organophosphates were both partitioned into benzene. The extract was passed through a bed of anhydrous sodium sulfate, then analyzed by gas chromatography. Chlorinated hydrocarbons were detected with ECD or HECD. Organophosphates were detected with nitrogen-phosphorus specific detector (NPD) or flame photometric detector (FPD). Analytical recoveries for all compounds were in excess of 95 percent.

## RESULTS

Analytical results are presented in Table 2. No samples had detectable residues of 1,3-dichloropropene at a minimum detectable level (MDL) of 0.1 ppb. No residues of chloroallyl alcohol were detected at a MDL of 0.6 ppb. No residues of chlorinated hydrocarbons or organophosphates were detected at a MDL of 5.0 ppb. A total of 54 wells were monitored for residues of 1,3-dichloropropene, 27 organophosphates and 22 chlorinated hydrocarbons. A total of 8 wells were monitored for the presence of chloroallyl alcohol.

## DISCUSSION

Cis- and trans-1,3-dichloropropenes reportedly have a soil half-life of approximately 4 weeks as indicated by laboratory studies (ROBERTS and STOYDIN, 1976). Dichloropropenes are readily hydrolyzed, in moist soils, to cis- and trans-chloroallyl alcohols (CASTRO and BELSER, 1966). Dichloropropenes disappear in sandy soils at 15-20° C (in closed containers) at a rate of 2-3.5 percent a day. In clay-containing soils, this rate could increase to as much as 25% a day (VAN DIJK, 1974). Chloroallyl alcohols disappear (in sandy soils at 15° C) 4.5 times as fast as the parent dichloropropenes for the cis-isomer, and 6.5-12 times as fast for the trans-isomer (VAN DIJK, 1974). Degradation of chloroallyl alcohols is initiated by microbial dehalogenation (BELSER and CASTRO, 1971). Chloroallyl alcohols are reported to be strongly bound to soil components (ROBERTS and STOYDIN, 1976).

Data from this study indicate that the cis- and trans-1,3-dichloropropenes, cis- and trans-chloroallyl alcohols, 27 organophosphates and 22 chlorinated hydrocarbons have not migrated into aquifers from which the sampled wells draw their water supplies. Since nearly all of these pesticides have been used in the studied areas for over 15 years, it appears that sufficient degradation in the soil profile or adsorption to soil components have occurred to prevent groundwater contamination.

TABLE 1

### PHYSICAL DATA FOR SAMPLED WELLS

<u>Location</u>	<u>Depth (ft)</u>	Type m - municipal p - private
1. Ripon	158	m
2. Ripon	300	m
3. Ripon	200	m
4. Manteca	370	m
5. Manteca	207	m
6. Raymus Village	295	m
7. Livingston	-	m
8. Livingston	-	m

TABLE 1 (Continued)

PHYSICAL DATA FOR SAMPLED WELLS

<u>Location</u>	<u>Depth (ft)</u>	Type m - municipal p - private
9. Atwater	320	m
10. Hilmar	-	m
11. Hilmar	-	m
12. Merced	133	m
13. Merced	155	m
14. Winton	-	m
15. Castle AFB	300	m
16. Delhi	273	m
17. Tranquility	450	m
18. Caruthers	-	m
19. Mendota	150	m
20. San Joaquin	600	m
21. San Joaquin	600	m
22. Selma	120	m
23. Parlier	180	m
24. West Parlier	250	m
25. Reedley	250	m
26. Fowler	177	m
27. Selma	260	m
28. Selma	180	m
29. Firebaugh	198	m
30. Firebaugh	185	m
31. Santa Maria	-	m
32. Santa Maria	-	m
33. Santa Maria	-	m
34. Guadalupe	-	m
35. Guadalupe	-	m
36. Lompoc	65	p
37. Lompoc	164	m
38. Lompoc	195	m
39. Santa Ynez	-	m
40. Edison	700	m
41. Edison	900	m
42. Lamont	-	m
43. Lamont	-	p
44. Lamont	200	p
45. Lamont	-	m
46. Lamont	700	m
47. Shafter	400	p
48. Shafter	400	p
49. Shafter	240	m
50. Shafter	675	p
51. Shafter	700	m
52. Shafter	600	m
53. Wasco	922	m
54. N. Kern	1200	m

Information on wells was obtained from representatives of the well system.

TABLE 2

ANALYTICAL RESULTS OF WATER SAMPLES

<u>Area (County)</u>	<u>Number of Wells Sampled</u>	<u>Number of Positives</u>		
		<u>1,3,-D</u>	<u>Organo-phosphates</u>	<u>Organo-chlorines</u>
San Joaquin	6	0	0	0
Merced	10	0	0	0
Fresno	14	0	0	0
Santa Barbara	9	0	0	0
Kern	15	0	0	0
Total	54	0	0	0

TABLE 3

Pesticides Detectable by Chlorinated Hydrocarbon Screening Method

Aldrin	Endrin
Botran (DCNA)	Heptachlor Epoxide
Captan	Hexachlorocyclohexane isomers (BHC) including Lindane
Chlordane	Kelthane (Dicofol)
Dacthal (DCPA)	Methoxychlor
DDD	PCNB
DDE	Perthane (Ethylan)
DDT	Tedion (Tetradifon)
Endosulfan I	Toxaphene
Endosulfan II	
Endosulfan III	

TABLE 4

Pesticides Detectable by Organophosphate Screening Method

Baytex (Fenthion)	Imidan (Phosmet)
Cygon (Dimethoate)	Malathion
Dasanit (Fensulothion)	Methyl Parathion
DEF	Methyl Trithion
Delnav	Parathion
Diazinon	Phosdrin (Mevinphos)
Di-Syston (Disulfoton) (parent only)	Phosphamidon
Dursban (Chlorpyrifos)	Supracide (Methidathion)
Dyfonate (Fonofos)	Thimet (Phorate) (parent only)
Dylox (Trichlorfon)	Torak (Dialifor)
EPN	Trithion (Carbophenthion)
Ethion	Zolone (Phosalone)
Folex (Merphos)	
Guthion (Azinphosmethyl)	

#### REFERENCES

- BAINES, R. C., L. J. KLOTZ, and T. A. DEWOLFE. *Phytopathol.* 67:936-940 (1977).
- BELSER, N. O. and C. E. CASTRO. *J. Agri. Food Chem.* 19:23-26 (1971).
- CASTRO, C. E. and N. O. BELSER. *J. Agri. Food Chem.* 14:69-70 (1966).
- NEUDECKER, T. A. STEFANI and D. HENSCHLER. *Experientia* 33:1084-1085 (1977).
- STOLZENBERG, S. H. and C. H. HINES. *Environ. Mutagen.* 2:59-66 (1980).
- ROBERTS, T. R. and G. STOYDIN. *Pestic. Sci.* 7:325-335 (1976).
- VAN DIJK, H. *Agro-Ecosystems* 1:193-204 (1974).